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(54) Title: DIREACTIVE MESOGENIC COMPOUNDS AND INTERMEDIATES

(57) Abstract

The invention relates to direactive mesogenic compounds or mixtures thereof comprising mesogene-containing molecule, said mesogens having two side chains attached thereto which contain a terminal polymerizable functional group, said mesogens and said functional groups being separated by at least two to twenty spacer atoms, wherein both spacer groups have different chain length.

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DIREACTIVE MESOGENIC COMPOUNDS AND INTERMEDIATES

The invention relates to

in the presence of a base, and

direactive mesogenic compounds or mixtures thereof obtainable by 5 a) treating a mesogenic diol of formula I, HO-MG-OH (1) 10 in which MG is a mesogenic group, with a mixture of the halids of formula II and III, 15 X1-(CH₂)_m-Ra (11) X2-(CH₂)_n-Rb (111) 20 in which are each independently CI, Br or J, X1 and X2 25 m and n are different integers between 1 and 20 Ra and Rb are each independently groups selected from -CH₂OH 10 -CH=CWH 30 wherein is H, CH3 or Cl,

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b) treating the resulting intermediate

- in the case of Ra and Rb being -CH₂OH, with a vinyl derivative of formula CH₂=CW-(CO)a-O- or a reactive derivative thereof, in which a is 0 or 1
- in the case of Ra and Rb being -CH=CWH with a perbenzoic acid.
- The invention furthermore relates to the preparation of such compounds and to their use in electrooptical scattering systems and for the preparation of oriented liquid crystal polymers.
- Reactive liquid crystal compounds can be polymerized in situ, whilst in their liquid crystal phase, to give highly crosslinked anisotropic films which can be used, for example, as polarizing beam splitters (see, for example, EP 0,428,213). Reactive liquid crystal compounds have furthermore been proposed for electrooptical scattering systems (see, for example, EP 0,451,905), cholesteric polarizers (e.g. EP 0,606,940) and compensation films for STN displays (e.g. EP 0,423,881).

Reactive liquid crystal diesters of formula

are mentioned in EP 0,261,712 (n=o), EP 0,331,233 (n=1). Reactive liquid crystal biphenyls of formula

are disclosed by EP 0,405,713.

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The International Patent application WO 93/22397 discloses a compound of formula

These reactive liquid crystalline compounds often exhibit, however, rather high melting points disadvantageous values of the birefringence and comparable narrow mesophase ranges.

In view of the broad range of applications of reactive liquid crystal compounds it was desirable to have available further compounds of this type which fulfill the various requirements such as a reasonably low melting point, a high birefringence, a broad mesogenic range and preferably an enantiotropic nematic range to a high degree.

It was an object of the present invention to provide new reactive liquid crystalline compounds with advantageous properties thus extending the pool of reactive liquid crystal compounds available to the expert. Other objects of the present invention can be taken from the following detailed specification.

The present invention thus relates to reactive mesogenic compounds or mixtures thereof obtainable by treating mesogenic diols of formula I, in particular those having a symetric structure unit with a mixture of halides of formula II and III and to their use in electrooptical systems of scattering type and for the preparation of oriented liquid crystal polymers. The invention furthermore relates to the preparation of compounds according to formula I.

Preferred embodiments of the present invention are:

 a) Composition of direactive compounds comprising at least one compound of each formula IV, V and VI,

$$R^{1}$$
-(CH_{2})_m-O-MG-O-(CH_{2})_n- R^{2}

R1--(CH₂)_m-O-MG-O-(CH₂)_m-R1

V

 $R^2-(CH_2)_n-O-MG-O-(CH_2)_n-R^2$

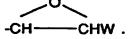
VI

5 in which MG, m and n have the meaning given, and

R1 and R2 are each independently

-CH₂-O-(CO)_a-CW=CH₂

or



b) Direactive compound or mixture thereof

in which

 $m - n \ge 1$, in particular 2, 3 or 4.

c) Direactive compound or mixture thereof in which

20 MG is a mesogenic group of formula VII,

-(A1-Z1)0-A2-

VIII

in which

A1 and A2 are each independently

- (a) 1,4-phenylene in which one or two CH groups may be replaced by N;
- (b) 1,4-cyclohexylene in which one or two nonadjacent CH₂ groups may be replaced by -O- or one -CH- group may be replaced by -C(CN)-;

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(c) naphthaline-2,6-diyl;

it being possible that group (a) is substituted by halogen cyano or alkyl, alkoxy or alkanoyl with 1 to 6 C atoms,

Z1 is each independently -COO-, -O-CO-, -CH₂-CH₂-, -C≡C-, -CH₂O-, -OCH₂- or a single bond, and

o is 1, 2 or 3.

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d) Direactive compound or mixture thereof in which MG is selected from the structure elements (1) to (6).

$$- \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - 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\underbrace{\left(\begin{array}{c} \left(\right) \\ \left(\right) \end{array}\right)}_{\left(\right) } - \underbrace{$$

in which

L is CH₃, Cl, F, OCH₃ or -CO-CH₃, and

r is 0, 1, 2 or 4.

e) Direactive compound or mixture thereof in which

n and m are given by the following table:

5 m 5 5 5 4 4 n 2 3 4 2 3

A further aspect of the present invention are direactive compounds of formula IV A

R1-(CH₂)_mO-MG-O-(CH₂)_n-R2

(IVA)

in which

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15 R₁ and R₂ have the meaning given,

m and n are different integers between 2 and 10, and

is a mesogenic group, the core of which being symmetrical, preferably a structure element of formula (1), (5) or (6), in particular

direactive compounds of the formula IVA1

25
$$R^{1}-(CH_{2})_{m}O \longrightarrow CO \longrightarrow CO \longrightarrow CO+(CH_{2})_{n}-R^{2} \qquad IVA1$$

30 in which

R1, R2,

L and r have the meaning given,

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m and n are different integers between 2 and 10, and

t is 0 or 1.

Another aspect of the invention are the polymers prepared by polymerizing a monomer according to any of the preceding claims and

a chemical intermediate compounds or mixtures thereof useful in preparing direactive compounds or mixtures thereof according to any of the claim 1 to 8, comprising mesogene-containing molecules, said mesogenes having two side chains attached thereto that contain hydroxyl or vinyl group at the end thereof, said mesogenes and said functional groups being separated by at least two to twenty spacer atoms, wherein both spacer groups have different chain length.

Above and below, the term reactive mesogenic compounds refers to reactive rod-like molecules which may be enantiotropic, monotropic or isotropic, preferably, however, enantiotropic or monotropic.

In the inventive compounds in which MG is a mesogenic group of formula VIII, A¹ and A² can be independently from each other an unsubstituted or a substituted 1,4-phenylene group of formula

$$X^2$$
 X^3
 X^5
 X^5

X2, X3, X5 and X6 can be independently from each other H, F, CI, methyl or CN.

In the following, for the sake of simplicity, the following notation will be used:

Phe. 2 X² 3 X³ 5 X⁵ 6 X⁶ is a 1,4-phenylene group carrying in 2-position the group X², in 3-position the group X³ etc.; in case X², X³, X⁵ and/or X⁶, denote H, this will not be specified in above notation, i.e. only true substitutions will be listed. Thus Phe, for example, is an unsubstituted 1,4-phenylene group while Phe.2F 5 CI is a 2-fluoro-5-chloro-1,4-phenylene group. Furthermore, Pyr is pyrimidine-2,5-diyl, Pyd is pyridine -2,5-diyl and Nap is a naphthalene-2,6-diyl group. The notation Pyr and Pyd in each case include the 2 possible positional isomers.

The compounds according to formula IV comprise 2- and 3-ring compounds (n=1 or 2) of formula IV2 and IV3:

$$R^{1}-(CH_{2})_{m}-O-A^{1}-Z^{1}-A^{2}-O-(CH_{2})_{n}-R^{2}$$
 IV2
 $R^{1}(CH_{2})_{m}-O-A^{1}-Z^{1}-A^{2}-O-(CH_{2})_{n}-R^{2}$ IV3

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In the 3-ring compounds of formula IV3, the ring groups A1 can be chosen independently from each other.

Especially preferred is a smaller group of 2-ring compounds exhibiting the following structures for -A1-Z1-A2-:

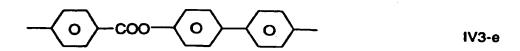
	-Phe.2CH₃-Phe-	IV2-1
	-Phe.3CH ₃ -Phe-	IV2-2
	-Phe.2Cl-Phe-	IV2-3
25	-Phe.3Cl-Phe-	IV2-4
	-Phe.2CN-Phe-	IV2-5
	-Phe.3CN-Phe-	IV2-6
	-Phe.2Cl3Cl-Phe-	IV2-7
	-Phe.2Cl3F-Phe-	IV2-8
30	-Phe.2F-Phe-	IV2-9
	-Phe.3F-Phe-	IV2-10
	-PhePhe-	IV2-11
	-Phe.F-Nap-	IV2-12
	-Phe.2Cl-Nap-	IV2-12
35	•	142-13

	-Phe.F-Nap-	IV2-14
	-Phe.3CI-Nap-	IV2-15
	-Phe.2F-Pyr-	IV2-16
	-Phe.2F-Pyr-	IV2-17
5	-Phe.2CH ₃ -Pyd-	IV2-18
	-Phe.2CI-Pyd-	IV2-19
	-Phe.F-CH2CH2-Phe-	IV2-20
	-Phe.3F-CH ₂ CH ₂ -Phe-	IV2-21
•	-Phe.2CI-CH ₂ CH ₂ -Phe-	IV2-22
10	-Phe.3CI-CH ₂ CH ₂ -Phe-	IV2-23
	-Phe.2CN-CH ₂ CH ₂ -Phe-	IV2-24
	-Phe.3CN-CH ₂ CH ₂ -Phe-	IV2-25
	-Phe.2Cl3Cl-CH ₂ CH ₂ -Phe-	IV2-26
	-Phe.2Cl3F-CH ₂ CH ₂ -Phe-	IV2-27
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The 3-ring compounds according to formula IV3 preferably exhibit the following structures for -A1-Z1-A1-Z1-A2:

$$- \left(\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \end{array} \end{array} \\ \begin{array}{c} \end{array} \end{array} \right) - \left(\begin{array}{c} \begin{array}{c} \\ \end{array} \end{array} \right) - \left(\begin{array}{c} \\ \end{array} \right$$

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In these structures, IV3-a to IV3-d, L¹ and L² denote independently from each other H, -Cl, -F, -CN and C_rH_{2r+1-s} and , in particular, -Cl, -F, -CN, -CH₃, and/or -C₂H₅.

Especially preferred are the following patterns:

	-Phe-Phe.2CH ₃ -Phe- -Phe-Phe.2Cl-Phe- -Phe-Phe.2CN-Phe-	IV3-a-1 IV3-a-2
15	-Phe-Phe.2F-Phe-	IV3-a-3 IV3-a-4
	-Phe-Phe-	1V3-a-4 1V3-a-5
	-Phe-Phe.2C₂H₅-Phe-	
		IV3-a-6
20	-Phe-Phe.3CH ₃ -Phe-	IV3-b-1
20	-Phe-Phe.3CI-Phe-	IV3-b-2
•	-Phe-Phe.3CN-Phe-	1V3-b-3
	-Phe-Phe.3F-Phe-	IV3-b-4
	-Phe-Phe.3C ₂ H ₅ -Phe-	IV3-b-5
25	-Phe.3F-Phe.3CI-Phe-	IV3-b-6
25	-Phe.3F-Phe.3CH ₃ -Phe-	IV3-b-7
	-Phe.3Cl-Phe.3Cl-Phe-	IV3-b-8
	-Phe.3Cl-Phe.3CH ₃ -Phe-	IV3-b-9
	-Phe-Phe.2Cl-Phe.3Cl-	IV3-b-10
	-Phe-Phe.3Cl-Phe.3Cl-	IV3-b-11
30	-Phe-Phe.2Cl-Phe.2Cl-	IV3-b-12
	-Phe-Phe.3Cl-Phe.2Cl-	IV3-b-13
	-Phe-Phe.2CH ₃ -Phe.3CI-	IV3-b-14
	-Phe-Phe.3CH ₃ -Phe.3CI-	IV3-b-15
35	-Phe-Phe.2CH ₃ -Phe.2CI-	IV3-b-16

-Phe-Phe.3CH ₃ -Phe.2Cl-	IV3-b-17
-Phe-Phe.2F-Phe.3CI-	IV3-b-18
-Phe-Phe.3F-Phe.3CI-	IV3-b-19
-Phe-Phe.2F-Phe.2CI-	IV3-b-20
-Phe-Phe.3F-Phe.2Cl-	IV3-b-21
-Phe-Phe.2Cl-Phe.3CN-	IV3-b-22
-Phe-Phe.3CI-Phe.3CN-	IV3-b-23
-Phe-Phe.2CI-Phe.2CN-	IV3-b-24
-Phe-Phe.3CI-Phe.2CN-	IV3-b-25
-Phe-Phe.2CH ₃ -Phe.3CN-	IV3-b-26
-Phe-Phe.3CH ₃ -Phe.3CN-	IV3-b-27
-Phe-Phe.2CH ₃ -Phe.2CN-	IV3-b-28
-Phe-Phe.3CH ₃ -Phe.2CN-	IV3-b-29
-Phe-Phe.3F-Phe.3CN-	IV3-b-30
-Phe-Phe.2F-Phe.3CN-	IV3-b-31
-Phe-Phe.3F-Phe.2CN-	IV3-b-32
-Phe-Phe.2F-Phe.2CN-	IV3-b-33
-Phe-Phe.2F-Phe.2F-	IV3-b-34
-Phe-Phe.3F-Phe.3F-	IV3-b-35
	•
-Phe-Phe.2CH ₃ -C ₂ H ₄ -Phe-	IV3-c-1
-Phe-Phe.2CI-C₂H₄-Phe-	IV3-c-2
-Phe-Phe.2CN-C₂H₄-Phe-	IV3-c-3
-Phe-Phe.2F-C₂H₄-Phe-	IV3-c-4
-Phe-Phe.2C₂H₅-C₂H₄-Phe-	IV3-c-5
-Phe-Phe.2Cl3F-C ₂ H ₄ -Phe-	IV3-c-6
-Phe-Phe.2Cl3Cl-C₂H₄-Phe-	IV3-c-7
-Phe-C ₂ H ₄ -Phe.2CH ₃ -C ₂ H ₄ -Phe-	IV3-c-8
-Phe-C ₂ H ₄ -Phe.2Cl-C ₂ H ₄ -Phe-	IV3-c-9
-Phe-C ₂ H ₄ -Phe.2CN-C ₂ H ₄ -Phe-	IV3-c-10
-Phe-C ₂ H ₄ -Phe.F-C ₂ H ₄ -Phe-	IV3-c-11
-Phe-C ₂ H ₄ -Phe.2OCF ₃ -C ₂ H ₄ -Phe-	IV3-c-12
-Phe-COO-Phe.OCO-Phe-	IV3-d-1
-Phe-COO-Phe.2CH ₃ -OCO-Phe-	IV3-d-2
	-Phe-Phe.2F-Phe.3CIPhe-Phe.2F-Phe.2CIPhe-Phe.3F-Phe.2CIPhe-Phe.3F-Phe.2CIPhe-Phe.3CI-Phe.3CNPhe-Phe.3CI-Phe.3CNPhe-Phe.3CI-Phe.2CNPhe-Phe.3CI-Phe.2CNPhe-Phe.3CI-Phe.3CNPhe-Phe.3CH ₃ -Phe.3CNPhe-Phe.3CH ₃ -Phe.3CNPhe-Phe.3CH ₃ -Phe.2CNPhe-Phe.3F-Phe.3CNPhe-Phe.3F-Phe.3CNPhe-Phe.2F-Phe.3CNPhe-Phe.2F-Phe.3FPhe-Phe.2F-Phe.3FPhe-Phe.2F-Phe.3FPhe-Phe.2CI-C ₂ H ₄ -PhePhe-Phe.2CN-C ₂ H ₄ -PhePhe-Phe.2CI ₃ -C ₂ H ₄ -PhePhe-C ₂ H ₄ -Phe-

	-Phe-COO-Phe.3CH ₃ -OCO-Phe-	IV3-d-3
	-Phe-COO-Phe.2CH ₃ 3CH ₃ -OCO-Phe-	IV3-d-4
	-Phe-COO-Phe.2OCH ₃ -OCO-Phe-	IV3-d-5
	-Phe-COO-Phe.2Cl-OCO-Phe-	IV3-d-6
5	-Phe-COO-Phe.2F-OCO-Phe-	IV3-d-7
	-Phe-COO-Phe.2F3F-OCO-Phe-	IV3-d-8
·	-Phe-COO-PhePhe-	IV3-e-1
	-Phe-COO-Phe.2FPhe-	IV3-e-2
10	-Phe-COO-Phe.3FPhe-	IV3-e-3
	-Phe-COO-PhePhe.2F-	IV3-e-4
	-Phe-COO-PhePhe.3F-	IV3-e-5
	-Phe.2F-COO-PhePhe-	IV3-e-6
•	-Phe.3F-COO-PhePhe-	IV3-e-7

It was observed that the stability of 3-ring compounds wherein one of the 2 groups Z1 is -COO- or -OCO- while the other denotes a single bond, can be increased if the compound is laterally di- or higher substituted, particularly di-substituted by -Cl, -F, -CN and/or -CH₃. Compounds of this type are preferred.

Especially preferred are further 3-ring compounds where both groups Z¹ are either -COO-, or -OCO- and at least one of the rings A¹, A¹ and A² are at least mono substituted.

In the compounds of formula IV R1 is CH2 = CW-COO-CH2-, CH2 =

CH-O-CH₂-, HW-C-C-, with W being H, Cl or alkyl with 1-5 C atoms and m being 1-7.

Preferably, R¹ and R² is a vinyl group, an acrylate group, an epoxy group and especially preferred are the following means of R¹ and R²:

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CH₂=C-COO-CH₂-

R1-2

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R1-3

CH₂=CH-O-CH₂-

ĊI

R1-4

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R1-5

with alkyl denoting C₁-C₃-alkyl and m being 1-5.

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The reaction methods mentioned are briefly summarized in the following synthetic tree:

Scheme I

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HO-MG-OH

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Mixture of Br-(CH₂)_m,-OH/Br-(CH₂)_n-OH
Butanone, K₂CO₃, heat

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 $HO-(CH_2)_m O-MG-O-(CH_2)_m-OH$ $HO-(CH_2)_m O-MG-O-(CH_2)_n-OH$ $HO-(CH_2)_n O-MG-O-(CH_2)_n-OH$

Mixture

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Butylvinyl ether DCM
1,10-Phenanthroline
Pd (II)-Acetate

CH₂ = CW-COCI

Mixture of "diacrylates"

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Mixture of "Divinylethers"

DCM = dichloromethane

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Scheme II

HO-MG-OH

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Mixture of Br-(CH₂)_m-CH=CH₂ Br-(CH₂)_n-CH=CH₂ butanone, K₂CO₃, heat

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Scheme III

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$$HO \longrightarrow CH_2 = CH - (CH_2)m - O \longrightarrow Br$$

Br-(CH₂)_m-CH=CH₂ butanone K₂CO₃, heat

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Br-O-O-(CH₂)n-CH=CH₂

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Certain compounds or mixtures according to the invention are obtainable in a "one-pot-synthesis" as outlined in scheme IV:

5 Scheme IV

1) TFAA/DCM

2) TEA/DCM

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$$CH_2=CH-CO_2-(CH_2)_m-O-Phe-COO-O-O-OCO-Phe-O-(CH_2)_m-OCO-CH=CH_2$$
 $CH_2=CH-CO_2-(CH_2)_n-O-Phe-COO-O-O-OCO-Phe-O-(CH_2)_m-OCO-CH=CH_2$
 $CH_2=CH-CO_2-(CH_2)_n-O-Phe-COO-O-O-OCO-Phe-O-(CH_2)_n-OCO-CH=CH_2$

TFAA = trifluoroacetic acid TEA = triethylamine

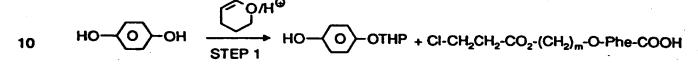
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Individual compounds of this type can be obtained according to schemes V to VII:

5 Scheme V



CI-CH₂CH₂-CO₂-(CH₂)_n-O-Phe-COOH

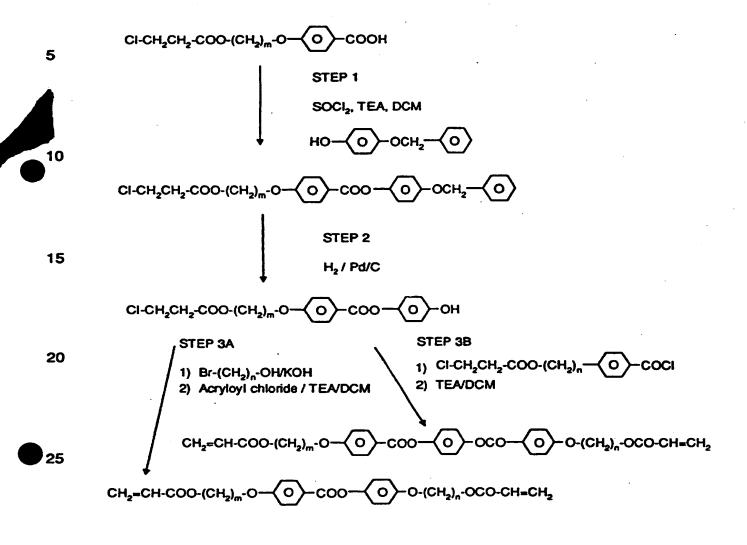
1) TFAA / DCM
2) TEA / DCM

2) TEA/DCM STEP 3

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Scheme VI



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Scheme VII

5 HO O O O OH (obtained according to WO 93/22397)

HO-(CH₂)_m-Br / K₂CO₃ / butanone HO-(CH₂)_n-Br

mixture of four homologous

20 mixture of four homologous

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The reaction schemes mentioned above are to illustrate the invention without restricting it. The expert can choose other reaction methods without any inventive efforts.

In the following and in the preceding, all percentages given are percentages by weight. Temperatures are given in degrees Celsuis.

The following examples are intended to illustrate the invention without restricting it.

Example 1

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The reactive liquid crystalline compound (1)

is prepared via the sequence of reaction steps shown in scheme V. In step 4 of scheme V 2.2 moles TFAA are added dropwise to a solution 2 moles of the phenol obtained in step 3 of scheme V and 2 moles of the benzoic acid in 2 I of DCM.

The reaction mixture is stirred at room temperature for 16 hours. Then 5 moles of TEA in 1 l of DCM are added. The mixture is stirred for 16 hours. Aqueous work-up and column chromatography give (1) which shows K 111 S.

The following compounds are obtained analogously:

Compound No.	m	n	phase transition temperatures (°C)
(2)	3	5	K 76 N 160 I
(3)	4	5	K 67 N 165 I
(4)	4	6	K 78 S 82 N 159 I
(5)	5	6	K 78 S 80 N 162 I
Comp 1	4	4	K 105 N 164 I
Comp 2	5	5	K 91 N 167 I
Comp 3	6	6	K 105 (S 95) 152 I

Example 2

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A mixture of 1 mol CI-CH₂CH₂-COO-(CH₂)₄-O-O-COOH,

1 mol CI-CH₂CH₂-COO-(CH₂)₄-O—O COOH, and 1 mol p-hydroquinone is treated with 22 moles of TFAA followed by 2.5 moles of TEA.

A mixture consisting of 1 part comp 1 and 1 part comp 3 and 2 parts of Compound No. (4) is obtained which shows a melting point of 56 °C and a clearing point of 163 °C.

Analogously a mixture of the following compounds is obtained:

	<u> </u>	m	parts
30	3	3	1
	6	6	. 1
	3	6	1
	6	3	1

This composition shows a melting point below 30 °C and a clearing point of 119 °C.

Example 3

A mixture of 0.5 moles of biphenol, 1.3 moles of potassium hydroxide, 0.6 moles of 3-bromopropanol and 0.6 moles of 3 bromohexanol is heated in 2 litres of butanone for 16 hrs. After aqueous work-up a mixture of

1 part of

1 part of

$$HO-(CH_2)_6-O-(O)-O-(CH_2)_6-OH$$
, and

2 parts of

is obtained.

This mixture is treated with 1.2 moles of acryloyl chloride and 1.2 moles of TEA in 1.5 litres of dichloroethane DCM and refluxed for 3 hours.

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After aqueous work-up the resulting reactionmixture is purified by column-chromatography to yield a mixture of diacrylates (6), (7) and (8).

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Compound No.	<u></u>	<u> </u>	parts
(6)	3	3	1
(7)	5	6	1
(8)	3	6	2

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Analogously a mixture of compounds of formulae (9), (10), (11) and (12) is obtained

	Compound No.	m	n	parts
	(9)	3	3 ,	1
	(10)	6	6	1
5	(11)	3	6	1
	(12)	6	3	1

Claims

Direactive mesogenic compounds or mixtures thereof obtainable
 by

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a) treating a mesogenic diol of formula I,

HO-MG-OH

(1)

in which

MG

is a mesogenic group,

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with a mixture of the halids of formula II and III,

(11)

(111)

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in which

X1 and X2 are each independently CI, Br or J,

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m and n are different integers between 1 and 20

Ra and Rb are each independently groups selected from

-CH₂OH

Ωſ

-CH=CWH

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wherein

W

is H, CH₃ or Cl,

in the presence of a base, and

b) treating the resulting intermediate

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in the case of R³ and R⁵ being -CH₂OH, with a vinyl derivative of formula CH₂=CW-(CO)₃-O- or a reactive derivative thereof, in which a is 0 or 1

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- in the case of Ra and Rabeing -CH=CWH with a perbenzoic acid.
- Composition of direactive compounds comprising at least one compound of each formula IV, V and VI,

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N

V

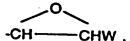
VI

in which MG, m and n have the meaning given, and

R1 and R2 are each independently

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or



3. Direactive compound or mixture thereof according to claim 1 or 2

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in which

 $m - n \ge 1$.

4. Direactive compound or mixture thereof according to any of the preceding claim in which

MG is a mesogenic group of formula VII,

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-(A1-Z1)₀-A2-

VIII

in which

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A1 and A2 are each independently

- (a) 1,4-phenylene in which one or two CH groups may be replaced by N;
- (b) 1,4-cyclohexylene in which one or two nonadjacent CH₂ groups may be replaced by -O- or one -CH- group may be replaced by -C(CN)-;
- (c) naphthaline-2,6-diyl;

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it being possible that group (a) is substituted by halogen cyano or alkyl with 1 to 6 C atoms,

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- Z¹ is each independently -COO-, -O-CO-, -CH₂-CH₂-, -C≡C-, -CH₂O-, -OCH₂- or a single bond, and
- o is 1, 2 or 3.

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 Direactive compound or mixture thereof according to any of the preceding claims in which MG is selected from

in which

L is CH₃, Cl, F, OCH₃ or -CO-CH₃, and

r is 0, 1, 2 or 4.

6. Direactive compound or mixture thereof according to any of the preceding claims in which

n and m are given by the following table:

m 5 5 5 4 4 n 2 3 4 2 3 7. Direactive compound of formula IV A

R1-(CH₂)_mO-MG-O-(CH₂)_n-R2

(IVA)

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in which

R1 and R2 have the meaning given,

m and n are different integers between 2 and 10, and

MG is a mesogenic group, the core of which being symmetrical.

8. Direactive compound according to claim 7 of the formula IVA1

$$R^{1}-(CH_{2})_{m}O$$
 O $CCH_{2})_{n}$ O $CCH_{2})_{n}$ CCH_{2} $CCH_$

in which

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R1, R2,

Land r have the meaning given,

m and n are different integers between 2 and 10, and

t is 0 or 1.

- Polymers prepared by polymerizing a monomer according to any of the preceding claims.
- 10. Chemical intermediate compounds or mixtures thereof useful in preparing direactive compounds or mixtures thereof according to any of the claim 1 to 8, comprising mesogene-containing molecules, said mesogenes having two side chains attached thereto

that contain hydroxyl or vinyl group at the end thereof, said mesogenes and said functional groups being separated by at least two to twenty spacer atoms, wherein both spacer groups have different chain length.

INTERNATIONAL SEARCH REPORT

Int- stonal Application No Pui/EP 96/00240

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C09K19/20 C09K19/12 C08F20/10 C07C69/92 C07C43/23

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 6 C09K C07C C08F

C09K19/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
x	WO,A,93 22397 (MERCK PATENT GMBH) 11 November 1993 cited in the application see the whole document and particularly example 4.1	1-10
X	GB,A,2 280 445 (MERCK PATENT GMBH) 1 February 1995 see claims 1-15	1-9
Y	EP,A,0 261 712 (N.V. PHILIPS' GLOEILAMPENFABRIKEN) 30 March 1988 cited in the application see the whole document	1-9

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the
ments, such combination being obvious to a person services in the art.
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Further documents are listed in the continuation of box C.

X Patent family members are listed in annex.



In stional Application No Full/EP 96/00240

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